MARTIN MARIETTA

ORTR

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December 21, 1984

Department of Energy
Oak Ridge Operations
Attention: Mr. H. Wayne Hibbitts
Office of Assistant Manager
for Safety and Environment
Post Office Box E
Oak Ridge, Tennessee 37831

Gentlemen:

Oak Ridge Task Force: Supplemental Work Statement on Mercury Methylation Study

Enclosed for your review and consideration is the work statement entitled "Experimental Studies on Mercury in Sediment and Floodplain Deposits From East Fork Poplar Creek: Methylation, Transport, and Biological Uptake." This work statement is in addition to ongoing studies and was requested by the ORTF.

There has been considerable discussion about the fate of mercury in the floodplain and sediments of East Fork Poplar Creek. In particular, concerns were expressed about the methylation of inorganic forms of mercury in the environs and the subsequent occurrence of methyl mercury in fish. The purpose of the proposed study is to investigate the potential transfer of mercury from sediments to aquatic biota.

If you have any questions about the content of the work statement, or if we can provide you with additional information, please let me know.

Sincerely,

K. E. Cowser

Kenneth E. Cowser
Enviroment, Safety, and Health

KEC:jct

Enclosure

cc: B. G. Blaylock
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EXPERIMENTAL STUDIES ON MERCURY IN SEDIMENT AND FLOODPLAIN DEPOSITS FROM EAST FORK POPLAR CREEK: METHYLATION, TRANSPORT, AND BIOLOGICAL UPTAKE

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Introduction

Inorganic mercury released into the aquatic environment is believed to accumulate in the sediments where it is methylated biologically (e.g., by bacteria) or abiotically (e.g., alkylated); thus, becoming available to fish and other organisms. This hypothesis is substantiated by the fact that most of the mercury released into aquatic environments is inorganic mercury but, of the total amount of mercury in fish, more than 90 percent is usually methylmercury. Although this hypothesis is generally accepted, there are still unanswered questions concerning the methylation of mercury.

Methylmercury is detected in water or sediments at exceedingly low concentrations. Furthermore, it is difficult to identify the precise location(s) where methylation takes place. As many, if not more, bacteria demethylate mercury in aquatic sediments as methylate mercury. Although the net rate of methylation is considered to be very low (less than 3 percent per year), the actual net rate of methylation of mercury is difficult to predict. Some evidence indicates that disturbing or dredging sediments will increase the methylation rate; however, information regarding the methylation of mercury in sediments is not well documented. Sites other than sediments where methylation may occur include: benthic invertebrates, fish, bacteria in the gut or gut contents of fish, and the water column.

Sediments in the East Fork Poplar Creek (EFPC) exhibit high levels of mercury (more than 300 ppm in some locations) which are traceable to releases from the Y-12 plant. Mercury continues to escape from Y-12 but in much smaller quantities than in the past. Quantitatively, most

of the Hg currently discharged from Y-12 is associated with suspen matter and not with the soluble phase of the effluents.

High levels of mercury (up to 2000 ppm) are present in the floodplain of EFPC as a result of past depositions. Large areas of the floodplain are perforated with crayfish tunnels that lead to the groundwater and subsequently to EFPC. These crayfish burrows may enhance conditions through the introduction of organic matter utilized in the methylation of mercury and may provide a hydrologic connection from floodplain to the stream. This situation presents another problem: If mercury releases at Y-12 are eliminated and the contaminated sediments in the stream are removed or isolated, will the mercury-laden floodplain contribute significant mercury to EFPC? What remedial action should be considered for this potential problem?

The purpose of the task described here is to address some of the questions outlined above by pursuing the following objectives:

1. Determine the contribution that sediments and floodplain deposits in EFPC make to the concentration of mercury in fish and other aquatic biota.
2. Determine the rate at which fish in EFPC accumulate mercury.
3. Determine whether direct contact with the sediments is necessary for fish to accumulate significant levels of mercury.
4. Determine, in so far as possible, the chemical species of mercury in sediments, floodplain deposits, and stream water.
5. Determine rates of Hg methylation in sediments, floodplain deposits, and stream water.

The experimental work will be conducted at the Environmental Sciences Facilities at the Oak Ridge National Laboratory. TVA personnel will assist in experimental design, in the experimentation and modeling activities related to data analysis.

In-Situ Studies

Two field studies will be conducted to determine the rate at which fish in the EFPC accumulate mercury. The results will also serve as a benchmark to be compared with those of future studies for the evaluation of remedial actions that may be taken in EFPC. The two studies are described as follows:

Enclosure Studies

Bluegill (Lepomis macrochirus) and/or redbreast sunfish (Lepomis auritus) will be placed in enclosures at different locations in EFPC. Some enclosures will be located below the West End Treatment Plant to ascertain whether conditions below the plant's outfall influence the accumulation of mercury in fish. Fish will be removed from the enclosure at appropriate intervals and analyzed. Most analyses will be limited to total mercury; however, some fish will also be analyzed for methylmercury. The advantages of such studies are that fish can be maintained in one area where the concentration of mercury in the water and sediment can be determined. Possible problems that can be encountered in such studies are: (1) maintaining fish in an enclosure for a long period of time, (2) influence of confinement on growth and rate of the accumulation of mercury, (3) maintaining fish in enclosures

under high water conditions, and (4) vandalism at uncontrolled sites. Because of these problems the following experiment will be conducted to complement information obtained from the above study.

Release and Capture Studies

East Fork of Poplar Creek below New Hope Pond will be stocked with uncontaminated, tagged bluegill and/or sunfish (with only background mercury levels. These fish will be recaptured in EFPC at appropriate intervals by electrofishing. Most fish will be analyzed only for total mercury; however, some fish will be analyzed for methylmercury to establish a quantitative relationship between methylmercury and total mercury. The advantage of this study over that of the former is that the fish will be exposed to the same conditions as existing fish in the stream and should exhibit similar growth rates and rates of mercury accumulation. The disadvantage is that the stocked population of fish may move out of the stream. As a result, there is always a risk that a sufficient number of marked fish will not be recaptured over a long period of time.

Artificial Streams

Artificial stream studies will be conducted with floodplain soils to determine whether floodplain deposits of mercury contribute to the concentration of mercury in fish and other biota. Floodplain deposits from EFPC will be placed in the upper end of artificial streams at the X-10 facilities of the Environmental Sciences Division. The deposits will be arranged in such a way that water percolates through the

deposits and then flows over a rocky substrate before entering a tank. The stream portion, which will not support a fish population, will be populated with invertebrates typical of EFPC and bluegill will be placed in a downstream tank. Flow may be augmented downstream of the floodplain deposits if sufficient flow cannot be maintained through the deposits. This experiment will allow the mercury contribution of floodplain deposits to be estimated separately from the mercury from creek sediments.

Experimental Ponds

Experimental ponds will produce conditions that should be favorable to the methylation of mercury in sediments. The ponds will also permit controlled investigations to determine the extent to which fish must be in direct contact with sediment in order to accumulate methyl mercury. Furthermore, the radiotracer ^{203}Hg will enable the quantification of fates of transfer of mercury within all trophic levels and abiotic compartments of the pond ecosystem. These transfer rates can be applied in the development of predictive models for the behavior and fate of mercury in aquatic systems.

Mercury-laden sediments from EFPC will be placed to a depth of 20 cm in four small experimental ponds at the X-10 facilities of the Environmental Sciences Division. The concentration and species, insofar as possible, of mercury in the sediments will be determined prior to removing the sediments from EFPC. Favorable conditions for methylation will be produced by the enclosed nature of the system, the ability to control pH to levels approaching 6.5, and absence of

dissolved oxygen within the interstital water of the pond sediments. After the ponds have developed a natural community of organisms, different age classes of bluegill and Gambusia affinis (mosquito fish) will be added to the ponds. In addition to the free-swimming fish, some fish will be confined to cages suspended above the sediments. Fish, water, various biota, and sediments will be sampled periodically to determine the concentration of mercury in different components of the ponds.

Two of the experimental ponds will be tagged with the radioactive tracer ^{203}Hg (half-life 61 d). This radioactive isotope of mercury has several advantages: it can be detected at very low concentrations, it can be measured quickly and easily, and it permits whole-body counting of live fish which reduces destructive sampling. Data from the tracer study will be compared with results of chemical analyses of samples for different forms of mercury to determine whether the ^{203}Hg follows the same pathway as the mercury incorporated in the sediments.

Sites for Hg Speciation and Rate Studies

Five sites on EFPC and two sites on the Clinch River will be used to characterize chemical species of mercury and for "in situ" determination of rates of methylation. The proposed sites are as follows:

New Hope Pond (Mile 14.6)

NOAA/ATDL Creek and Floodplain (Mile 13.6)

Wayne Clark Creek and Floodplain (Mile 10.9)

Above Sewage Treatment Plant (Mile 9.0)

Below Sewage Treatment Plant (Mile 4.8)

Cove at Clinch River Mile 6.8

Cove at Clinch River Mile 25.0 (Control Site)

Speciation

Mercury in EFPC water, suspended matter, sediments and floodplain deposits will be analyzed to determine different chemical species insofar as analytical methods are available. Mercury in water samples will be analyzed as total, dissolved (0.2 μm filters) and methyl forms. Total and dissolved mercury will be analyzed using the EPA method (USEPA 1979). Methyl mercury in water will be determined using the method of Futurani and Rudd (1980). This method involves liquid-liquid extraction followed by gas chromatography and has a reported detection limit of 0.0002 μg/L. As appropriate, other methods of analyzing forms of mercury in water may be used (e.g., Goulden and Anthony 1980).

Because EPA has proposed measuring "active" mercury (defined operationally by acidifying the aqueous sample to pH = 4 with nitric acid and then measuring mercury that passes through a 0.45 mm membrane filter) in the latest (8/29/83) draft of Ambient Water Quality Criteria for Mercury, (Section B), we will also measure "active" mercury in water samples from EFPC and from the pond and artificial stream experiments. Suspended matter from EFPC will be concentrated by continuous centrifugation of large volume water samples. Because only small samples will be obtained only total mercury and methyl mercury will be routinely measured in suspended matter. Selective extractants

(discussed subsequently) will be applied to suspended matter where sufficient material is available. Sediment and floodplain deposits will be fractionated both physically (size and density distribution) and chemically (selective chemical extraction and compound identification). Size and density fractions will be analyzed for total mercury to determine how mercury is distributed among these fractions. Selective chemical extractants may be applied to some size and/or density fractions. Unfractionated samples will be subjected to a battery of sequential chemical extractions which are used operationally to define how mercury is bound. The proposed sequential scheme is summarized in the following:

Step I: Exchangeable Hg - 1 M ammonium acetate, pH 7, solid/solution ratio 1:20, 2 hrs. shaking.

Step II: Easily reducible phase (bound to Mn oxides, partly amorphous Fe oxyhydrates) and carbonate phases - 0.1 M $NH_2OH \cdot HC\ell$ + 0.01 M $NH_2OH \cdot HC\ell$ + 0.01 M HNO_3, pH 2, dilution 1:100, 12 hrs. shaking.

Step III: Moderately reducible phases (e.g., poorly crystallized Fe oxyhydrates) - 0.2 M ammonium oxalate + 0.2 M oxalic acid, pH 3, dilution factor 1:100, 24 hrs. shaking.

Step IV: Organic fraction, including sulfide - 30% H_2O_2 + HNO_3, pH 2, 85°C, extracted with 1 M ammonium acetate, dilution factor 1:100, 24 hrs. shaking.

Step V: Residual fraction - conc. HNO_3, 180°C, 1:100

These, or similar, extractants have been widely used to characterize the partitioning of pollutant metals, including Hg in sediments, and thus form one basis for comparison of deposits in EFPC with deposits at other Hg-contaminated sites in the United States and elsewhere. Preliminary work on the form of mercury in EFPC deposits by ORAU ("A preliminary report on the nature of soil-mercury contamination in the Oak Ridge Area" G. Gleason and C. Gist, October 1984) has suggested association of Hg with black soil particles which may be incompletely combusted coal or other organic residue. Application of selective chemical extractants to isolated black soil particles and to bulk soils will better define the biotic availability and environmental mobility of Hg in these deposits.

Rates of Methylation

The net rate of Hg methylation is determined by a number of factors, including most importantly, the concentration of Hg, temperature, dissolved oxygen levels, rates of microbial activity, organic content, and pH. Even in areas where net methylation rates are relatively high the net fractional conversion (percent of amount of inorganic Hg present) is low and results in methylmercury concentrations that are very low and often undetectable. Net rates of methylation have usually been measured by incubation of water, particulate matter, sediment or other material in sealed containers for several weeks and then extracting the accumulated methylmercury. Canadian researchers working on the Wabigoon-English River system in Ontario employed the radiotracer ^{203}Hg to estimate rates of

methylation (Futurani and Rudd 1980). This radiotracer technique has the advantage that Hg methylation can be detected with much greater sensitivity than with stable Hg incubations. Incubation periods are reduced to 4 days and only a small amount of Hg is added to samples. The main limitation of the method is that it is not a conventional radiotracer method. A tracer method requires that the mercury isotope added be in equilibrium with all Hg species in the sample. The method does allow for comparisons of methylating activity within the same compartment (i.e., water, suspended matter, bed sediment) but not among sites (e.g., NHP, EFPC). Because we are primarily interested in identifying the most important source areas within EFPC for methylmercury production, we will use the radiotracer method outlined by Futurani and Rudd (1980).

References

Futurani, A. and J.W.M. Rudd. 1980. Measurement of mercury methylation in lake water and sediment samples. Appl. Environ. Microbiol. 40:770-776.

Goulden, P. D., and D. H. Anthony. 1980. Chemical speciation of mercury in natural waters. Anal. Chim. Acta. 120:129-139.

USEPA. 1979. Manual of Analysis of Water and Wastes. EPA 600-4-79-020. U.S. Environmental Protection Agency, Cincinnati, Ohio.

Schedule

1/85	6/85	1/86	6/86	1/87
Review Literature				
Experimental Pond Study				
	In-situ Studies			
	Speciation and Rate Studies			

1/85 - 4/85 Literature Review (1972-1984)

Experimental Pond Studies

1/85	Place ^{203}Hg tagged sediments from EFPC in Pond
4/85	Place fish in ponds
4/85-5/86	Periodic sampling of experimental ponds
6/86	Complete data collection
9/86	Complete data analysis
12/86	Complete final report

Artificial Stream Studies

4/85	Obtain floodplain soil from EFPC
4/85	Prepare artificial streams for experimentation
5/85	Begin experiments with artificial streams
5/85-12/85	Periodic sampling of artificial stream systems
3/86	Complete data analysis
6/86	Complete report

In-Situ Studies

5/85	Intiate enclosure studies
5/85	Release tagged fish to EFPC
5/85-11/85	Periodic sampling of enclosure studies and stocked fish in EFPC
3/86	Complete data analysis and report

Speciation and Rate Studies

3/85	Initiate speciation and rate studies
6/85	Begin rate studies at selected sites
9/85	Complete speciation study
11/85	Complete rate studies
3/86	Complete data analysis and report

Budget

	1985	1986	1987
In-situ Studies			
MY	0.5	0.25	
Chemical analyses and equipment	20K	10K	
Subtotal	70K	35K	
Experimental Pond and Artificial Stream Studies			
MY	1.0	1.0	1.0
Chemical analyses, equipment and cost of obtaining EFPC sediment and soil	85K	15K	----
Subtotal	185K	115K	100K
Chemical Speciation and Rate Studies			
MY	0.75	0.5	
Chemical analyses and equipment	25K	10K	
Subtotal	100K	60K	
TOTAL	355K	210K	100K